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THE DETERMINATION OF TOTAL PLUTONIUM IN THE PRESENCE OF ALUMINUM

BY

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THE DETERMINATION OF TOTAL PLUTONIUM IN THE PRESENCE OF ALUMINUM

Introduction

The adoption of aluminum nitrate as salting agent in the Redox process made it imperative that a method be available for determining plutonium in the presence of aluminum. However, large amounts of aluminum have been found to interfere with the determination of plutonium by the lanthanum fluoride procedure. Previous attempts to increase the accuracy of the lanthanum fluoride method, by precipitating LaF_3 from 4 M HF (rather than 2 M), have been successful only when the initial plutonium level was high.

Summary

A method has been developed which permits greater than 96% plutonium recoveries from 1.5 M aluminum nitrate solutions. Quantitative carrying of plutonium (mixed oxidation states) on a lanthanum hydroxide--sodium diuranate precipitate serves to separate the plutonium from the aluminum as well as from any dichromate present. The precipitate, following washing with dilute caustic, is dissolved in 2 M HCl. A standard lanthanum fluoride procedure then follows. An outline of the complete procedure is included in this report.

Experimental

The effect of the amount of aluminum present on the plutonium recovery by the method herein described was investigated. Results of several analyses in which the aluminum concentration in the sample was varied are shown in Table I. These data indicate that, at least for samples moderately high in plutonium, the method will give good results when aluminum is as high as 1.5 M.

TABLE I

EFFECT OF ALUMINUM CONCENTRATION ON PLUTONIUM RECOVERY

Pu(IV) Present, d/m	Al Present, mg.	M Al 50 λ Sample	Pu * Carried, %
122,000	0.4	0.3	97.7
122,000	1.0	0.75	98.5
122,000	2.0	1.5	98.1

24 mg. U and 0.5 mg. La precipitated as hydroxide

* Count not corrected for self-absorption of sample

That the method works satisfactorily at low plutonium content is shown by the data in Table II. No studies have been made at very low ($<$ 1000 d/m) plutonium levels. A comparison of the data in Tables I and II indicates that the method works equally well with Pu(IV) and Pu(VI). No thorough investigation of the effect of varying the amount of uranium used as a carrier has been made. The data in Table III show that certainly no advantage is gained by using more than 4.8 mg. U (ca. 10 µl 2 M UNH). Although the exact amount of base added is not critical, one must be certain that enough is present to assure complexing of the aluminum ion and to completely precipitate the uranium as sodium diuranate.

TABLE II

EFFECT OF INITIAL PLUTONIUM ON PLUTONIUM RECOVERY

Pu(VI)Present, d/m	Al Present, mg.	Pu * Carried, %
6,170	2	96.8
15,400	2	96.5
31,600	2	99.3
45,700	2	95.8

24 mg. U and 0.5 mg. La precipitated as hydroxide

* Count not corrected for self-absorption of sample

TABLE III

EFFECT OF AMOUNT OF URANIUM PRECIPITATED

Pu Present, d/m	Al Present, mg.	U Precipitated, mg.	Pu * Carried, %
63,700	0	24	96.5
63,700	0.4	24	95.1
63,700	1.0	24	95.8
63,700	2.0	24	52.5+
63,700	2.0	4.8	98.5
63,700	2.0	4.8	96.8
63,700	2.0	4.8	97.4
63,700	2.0	4.8	101

\+ Probably insufficient base added

* Count not corrected for self-absorption of sample

Interferences

Dichromate, much in excess of that expected in process solutions, has no adverse effect on plutonium recovery. Analyses performed in the presence of 10^{-5} moles of $K_2Cr_2O_7$ (approximately 10 times that expected in process samples) gave an average plutonium recovery of 98.6 ± 1.4%. However, large quantities of Cr(III) do interfere in the procedure; the volume of the precipitate is reduced, the precipitation of sodium diuranate is greatly reduced or prevented, and plutonium is poorly carried. Plutonium recoveries of about 70% were obtained when analyses were performed in the presence of 2×10^{-5} moles of Cr(III). Basic oxidation of the Cr(III) to dichromate by H_2O_2 (added after the NaOH in Step 2 of the outline) followed by decomposition of the excess peroxide (heat in the presence of a Pt wire) serves to remove the interference. Plutonium recoveries of 98% were obtained in the presence of 2×10^{-5} moles of Cr(III) when this modification was used. Most of the uranium remains in solution after the peroxide oxidation, but enough is coprecipitated with the lanthanum hydroxide to color it orange. Potassium persulfate and sodium bismuthate were tried as alternate oxidants. The former was nearly as good as the peroxide while the latter was completely unsatisfactory. Persulfate would have the advantage over peroxide of not interfering with the precipitation of sodium diuranate.

Silver ion (more than ca. 0.2 mg.) interferes since it carries through the procedure to appear as silver chloride on the mounting disc. Alpha counting efficiency is lowered due to absorption by the silver chloride. By dissolving the alkaline precipitate with HNO_3 instead of HCl and using hydroxylamine-sulfate instead of the hydrochloride, the silver is not precipitated with the lanthanum fluoride. R. L. Moore has employed this modification satisfactorily on solutions containing silver ion.(1)

The lanthanum fluoride method gives poor results with hexone samples high in dichromate. Hydroxylamine reduces the dichromate to Cr(III) which interferes with the carrying of plutonium on LiF_3. The present method has been used satisfactorily on such samples. In this connection, it has been found advantageous to add a solubilizing agent, such as acetone, to the aqueous solution previous to adding the hexone sample. Creeping of the hexone on the test tube is thus avoided.

Conclusion

The method as outlined is suggested for plutonium determinations in solutions high in aluminum and/or dichromate. With suitable modifications the procedure may be used when large amounts of Cr(III) or of cations giving insoluble chlorides are present. The method has been used for a large number of determinations in this laboratory and has been found to give consistently good precision (± 2.3% at 99% limits) and accuracy (0 to -4%).

Procedure

1. Add sample to 500 ul of a solution containing 0.25 mg. La^{+++} and 10 µl of 2 M UNH.* Stir.
2. Add 1 ml. 3.5 M NaOH. Stir.+ Let stand 5 minutes. Centrifuge 5 minutes in a clinical centrifuge at full speed. Discard centrifugate.
3. Wash twice with 1 ml. portions of 0.01 M NaOH.+ Discard washes.
4. Add 1.5 ml. 2 M HCl and 300 µl of 10% H_2NOH HCl.# Stir and let stand 10 minutes.
5. Add 3 drops of 27 M HF. Stir and let stand 5 minutes.
6. Centrifuge as in (2). Discard centrifugate.
7. Wash twice with 1 ml. portions of 1 M HNO_3-- 1 M HF solution.

8. Transfer precipitate to Zapon-ringed 22 mm. Pt disc with 1 M HNO_3. Evaporate, flame and coat with collodion.
9. Count for α activity.

Notes:

* Add the UNH only if less than 10 mg. UNH is present in the aliquot of sample taken for analysis.

† Add H_2O_2 and heat while stirring with a Pt wire if a large amount of Cr(III) is present.

\+ A reprecipitation step has been used successfully to replace the two washings.

In case Ag^+ or other cations giving insoluble chlorides are present substitute HNO_3 for HCl and $H_2NOH\ H_2SO_4$ for H_2NOH HCl in this step.

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References

Fundamental data for this paper are in Research Notebooks of R. E. Burns (HW-2211-T) and G. B. Barton (HW-2469-T).

(1) HW-2707-T and HW-2410-T, Research Notebooks of R. L. Moore.